

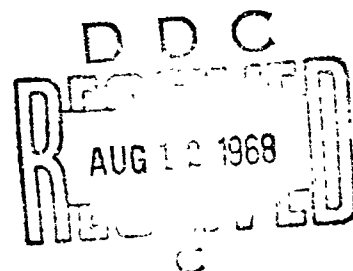
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Microporosity in Lead-Antimony Grid Alloys

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ABSTRACT

Microscopic examination of over two-thousand grid cross sections, which had been obtained from the product of many different manufacturers, indicated that grid microporosity was very high. Using magnification as low as 45X, microporosity was found in 20% of the grids by random sampling. Examination at higher magnification showed much more microporosity to be present, and it is estimated that 40 to 50% of the cross sections would have been found to be porous if examined at higher magnification (800-1000X). Since the sampling was random, it is very probable that all of the cast grids had porosity at one or more points which could contribute to premature failure by corrosion.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C05-14
Projects SF 013-06-03-4366
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MICROPOROSITY IN LEAD-ANTIMONY GRID ALLOYS

INTRODUCTION

Microporosity in grid castings is an old problem but one that has a particular significance to manufacturers and users of lead-acid storage batteries, because it is a source of corrosion in the grid castings used as an active material support and as an electrical conductor. In a previous report (1) reference was made to this relationship between microporosity and grid corrosion, but microporosity has not been considered more than an occasionally occurring phenomenon until the present investigation.

It has now been determined that microporosity is a general problem of considerable magnitude, which occurs wherever lead-antimony alloys are used as cast, without heat treatment or cold work. This generalization was made after examining a collection of NRL battery plate samples. These samples had been obtained from many manufacturers during the last decade.

Although the examination was, for the most part, confined to negative grids, a sufficient number of positive grids were also examined to confirm that the same degree of microporosity also occurred there. It was thus not a case, as was at first suspected, of less care being used in the casting of negative grids, simply because they receive less corrosive action than the positive grids. Further, conversations with representatives of several battery companies confirmed that the casting process is essentially automatic, and no differentiation is made between positive and negative grids in the casting process. It should be pointed out, however, that it is the practice in some cases to make the negative grid thinner than the positive grid which could increase the difficulty of obtaining nonporous castings.

The major emphasis was placed on a study of the negative grid rather than the positive grid for two reasons. First, by using the negative grid more samples were available for inspection, because new plates and plates that had been used in cycling tests or actual service could be studied, without the extensive corrosion and subsequent masking of the porous areas that would have been the case in similarly treated positive grids. Second, the negatives were being studied for other characteristics, and it required little additional effort to make a study of the grid sections in these samples that were already polished.

CONDITIONS OF THE EXAMINATION

Many samples were examined as a basis for this report. These samples, as said previously, were part of a collection of battery plate samples that had been accumulated at NRL during the past decade. Included in the collection were representative samples of plates made by many manufacturers, both in the U.S. and other countries. Also included were samples of plates in the different steps of manufacture and samples of plates that were removed during or following various types of operation or test.

The material used as samples had been obtained from the manufacturer in various forms—as individual plates, cell elements, parts of plates, or completely assembled batteries. In all cases the plates required further treatment to obtain samples suitable for

microscopic examination. If removed from the electrolyte and if a positive grid, the plate was dried without washing by repeated blotting on absorbent paper, followed by mild oven drying. Negative grids were usually washed and then dried, but in some cases samples were dried in an inert atmosphere without washing.

Strips were then cut from the carefully supported and clamped plate. These strips were taken from the plate with the long dimension parallel to the smaller grid bars, which are usually horizontally placed in the battery cell (Fig. 1). Such strips could be cut from the battery plate with very little distortion of the grid members, dislodgment of active material, or other damage, if an X-acto razor saw was used. Four or more strips, each approximately 1-1/4 in. wide by 1-3/4 in. long, from the same plate were usually placed together in one mold cavity, which was 1-1/2 in. diameter by 1-3/4 in. high.

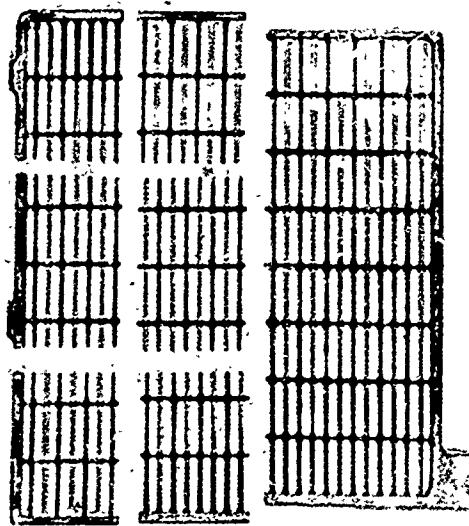


Fig. 1 - Sectioning of storage battery plates to obtain samples for microscopic examination. The active material which would normally fill the spaces between, and partially cover, these grids has been eliminated here for the sake of clarity. Photographed grid is also somewhat less than natural size.

The mold cavity served to hold the strips approximately in a vertical position, which was definitely insured by using a suitable support and separation for the strips. After a final 24-hour drying at 45°C, the strips were impregnated in the mold by filling it under vacuum, with a catalyzed, low-viscosity polyester. After the plastic had hardened, the cylinder of plastic was ejected. The cylinder then contained four or more strips of the plate, each with its long dimension parallel to the axis of the cylinder. The cylinder was cut into two 1-1/2-in.-diameter-by-7/8-in.-high pieces, effectively cross sectioning the plate at right angles to the plate surface. The height of each cylinder was further decreased by 1/8 to 1/4 in. during grinding and polishing.

The above description illustrates why the cross section finally available for microscopic examination was the result of completely random selection. But the areas which

had thus been selected were nevertheless at right angles to the plate surface and were placed as far as possible from any distortion or damage that might accompany the original cutting of the plate into strips.

This random sectioning usually resulted in sections where the smaller, staggered grids were seen in cross section, surrounded by the active material that made up the greater portion of the plate and cross section (Fig. 2). In the common starting, lighting, and ignition type battery the above preparation of a single cylindrical sample may present 20 to 30 individual grid cross sections for examination.

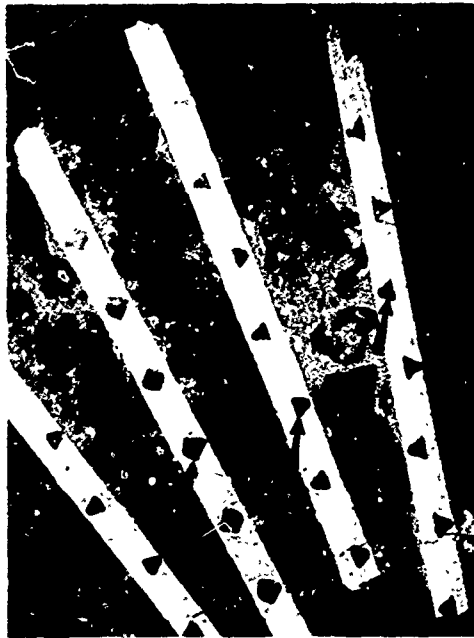


Fig. 2 - Appearance of samples, cut from the plate as in Fig. 1, after they had been impregnated with plastic, mounted, sectioned, and polished. The four slender, light-appearing, rectangular sections are cross sections through a cured but unformed plate. They are embedded in a cylindrical plastic casting, of which a portion of the perimeter can be seen at the top of the photograph. The arrows point to cross sections of the grid, as seen within the plate sections. The origination magnification was 3.2X.

It was also possible to obtain sections containing the full-width supporting bars, which are normally vertically placed in the battery cell. These were, of course, longitudinal sections of such bars and occupied almost the full width of the plate strip. If grinding was done carefully, it was possible to develop a longitudinal section such that it gave a plain indication of where the staggered sections intersected it, and the micro-porosity could be determined at such points.

The examination of all the grid sections depended on very careful polishing; since no subsequent etch treatment was used, the detection of detail depended on variation in hardness and reflectivity for the various components of the section. As a result of this type of polishing, the metal surface tends to show a slight concavity at regions where microporosity exists, as if the sample were somewhat softer at these points. Thus, although the individual pores could not be detected at low magnification, the presence of the concavity in the region could be seen, and the porosity could then be verified at these areas by examination at higher magnification. This relationship between concavity and microporosity made it possible to scan large areas of the sample fairly rapidly and to seek out and verify the presence of microporous areas.

Each grid cross section of a large number of samples was examined by this type of search. A tally was maintained of the number of cross sections examined and of the number of such grid-bar cross sections in which porosity was detected. The magnification used in this search was only 45X. Approximately 2000 grid-bar cross sections were examined, and 20% of these were found to have porosity that could be detected at the low magnification used. Examination at higher magnification invariably showed microporosity that had not been detected at the lower magnification used in the scanning. It was not feasible to make a detailed examination at the much higher magnifications (800-1000X) required to detect this less easily seen microporosity. However, it is estimated that if all of the grid sections had been examined at these high magnifications, the number found to be porous would have been increased to approximately 50%.

Practically every plate examined exhibited porosity by this random sectioning. A few grids had porosity that escaped detection at the lower magnification, but microporosity was found when the grids were examined at higher magnification. Most of the grids, regardless of manufacturer, seemed to average about the same porosity when examined in this way. There were one or two exceptions where the castings were found to be very bad, with about 50% of the grid-bar cross sections having porosity that could be detected at 45X.

DISCUSSION OF THE OBSERVATIONS

In a broad sense microporosity may be considered as any porosity that can be detected only by optical magnification. This definition of microporosity must include porosity resulting from every kind of defect—from gas inclusions to cold shuts formed as a result of a too low mold or melt temperature. Porosity that results from improper casting technique can usually be remedied by more careful attention to detail. Such a usage of the term microporosity is too general for the purpose of the present discussion.

There is another type of microporosity (that which is the subject of the present report) which is more insidious and much more difficult to eliminate. This type of microporosity is caused by the tendency of lead alloys (hypoeutectic) to supercool and for the lead to then rapidly grow extensive dendritic crystals in an effort to relieve this supercooling. In such a rapid crystal growth the lead precipitates in a relatively pure state, and the composition of these dendrites is unable to approach that required by the equilibrium phase diagram. The other alloying constituent is rejected at the dendritic boundaries, and this final portion remains liquid during a temperature drop of several degrees before it in turn solidifies. In the case of the lead-antimony alloys, this lower-temperature-freezing portion contains antimony in eutectic composition and possible impurities. Because of the complex structure generated by the dendritic crystals of lead and because the lead forms the major portion of the alloy, this remaining liquid portion is confined to relatively narrow and complex channels between the solidified dendritic crystals of lead. When the eutectic portion does freeze, the reduction in volume will be quite marked. At points where solidification begins practically simultaneously, crystallization of lead and antimony occurs, and the still liquid metal is withdrawn from other

areas to feed the process in a manner analogous to the shrinkage of mercury within a capillary during the lowering of temperature. If solidification begins at different points along the channels, there will be a shortage of metal at the last freezing portions. At these points voids will occur between the primary dendrites. Simultaneous nucleation at many points in the channels can, and does, result in numerous voids in the interdendritic channels and, in some cases, at grain boundaries. The foregoing description is oversimplified and does not fit with all points of actual observation, but it identifies the type of porosity with which this report will be mainly concerned.

Figure 3 illustrates the appearance of a grid cross section at the low magnification (45X) used in scanning for porosity. The bright portion is the grid, as seen when sectioned. The dark areas indicated by the arrows are locations of rather extensive porosity. The black area is not caused by a hole of equal size but is the result of a slightly concave surface at that point and of the effect that this produces on reflection from the surface. The slightly concave surface results when a fairly extensive area of micro-porosity occurs and is probably the result of the metal being removed somewhat faster during polishing in this area which is deficient in the harder antimony particles.



Fig. 3 - Magnified area of a grid section, similar to those seen in Fig. 2. The arrows point to dark, sunken areas in the grid that indicate porous areas. The original magnification was 45X. The superimposed line spacing represents 528 microns between lines.

An area similar to that in Fig. 3 is shown at a higher magnification (150X) in Fig. 4. As can be seen, the major portion of the photograph is occupied by only a small part of the total grid cross section. Surrounding this grid section on the right and at the bottom are portions of the active material of the plate section. The black areas in the active

material may either represent holes where the impregnating plastic did not penetrate or areas where the polishing has produced low spots (as in Fig. 3). Both effects look the same at this magnification and with this type of illumination.

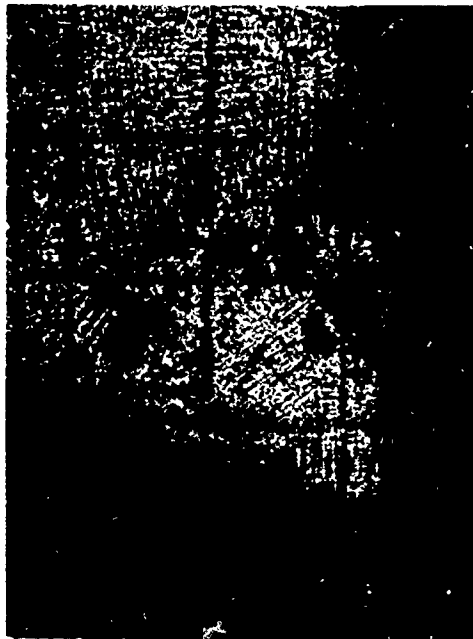


Fig. 4 - Further magnification of a grid cross section, showing a porous area. The parallel rows of bright lines seen in the grid section represent antimony particles which have segregated in the channels between primary dendrites. The dark areas within the grid represent porosity in the casting. The original magnification was 150X. The superimposed line spacing represents 158 microns between lines.

In the lighter area, which comprises the grid, the parallel rows of even brighter particles are caused by segregated crystals of antimony which have precipitated from the low-melting eutectic during final freezing. These brightest particles outline the positions of the channels that remained filled with eutectic after primary freezing of the lead dendrites. At certain points in the grid section dark voids can be seen. Careful inspection shows that these are oriented parallel to the primary dendrites and the associated rows of bright precipitated particles of antimony. This orientation becomes more obvious by reference to Fig. 5, which shows a portion of the same area further magnified to 400X. At this magnification it can be seen that the voids occur parallel to and between the primary lead dendrites (gray portions) and in line with the bright rows of antimony particles. These voids are thus related to the dendritic channels, and since they are wider than the rows of antimony particles, the antimony particles must only represent the median line of what was probably a much wider channel between the dendritic branches of the primary lead crystals. Many similar areas seen in different lead-antimony alloys and in plates from different companies leave no doubt that this type of microporosity does indeed follow the interdendritic channels and almost certainly must be the result of metal withdrawal from such areas in the final stage of solidification.



Fig. 5 - Further magnification of the same area as in Fig. 4. Note the parallel rows of bright antimony particles which show the positions of the channels between the primary dendrites; note also that voids (dark) align with these parallel rows of antimony particles. The original magnification was 400X. The superimposed line spacing represents 60 microns between lines.

Very little additional information can be obtained by further magnification. Figure 6, taken at 800X, shows only that the voids are clean and contain no corrosion product, oxide or dross inclusions, or similar evidence of the introduction of foreign substance that might cause porosity. When the microscope is racked up (inverted microscope), and thus focused on the bottom surfaces of the holes, it is possible to see that the bottom and sides of the hole are bright, with small pointed proturbances, which were probably the ends of dendritic primary crystals, exposed as the eutectic metal receded during final solidification. It is unlikely that gas inclusions would leave such proturbances, since metal would not grow into a gaseous medium. Although it is not easy to show in a photograph, it can also be proven that the holes were filled with plastic. This indicated that the porous area extended to the surface of the casting.

The area shown in Fig. 4 has porous portions both near the surface of the casting and at a considerable depth beneath the surface. This type of porosity was found to be so common that it was not included in the porosity count previously mentioned. If this surface or near-surface porosity had been included in the count, the percentage of porous grids would have been much higher. Also, it was not counted because it was not easily detected at 45X magnification and did not appear to extend deep enough into the sample to present a significant corrosion problem, unless it could initiate a stress corrosion attack such as has been reported previously (1). This near-surface microporosity of the grid usually did not extend around the entire circumference but appeared at one or more points. This type of porosity occurred to a varying depth and with a greater or less severity in samples from different sources.

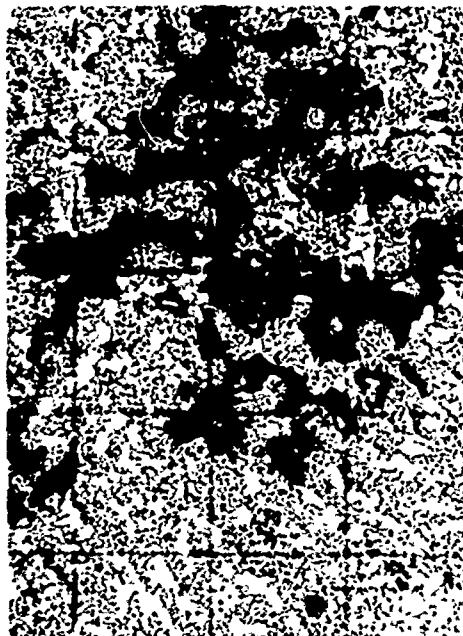


Fig. 6 - Further magnification of a portion of the area shown in Fig. 5. Voids are filled with a clear impregnating plastic, but there is no evidence of oxide or dross inclusions or other contaminant. The slight flare seen in some portions of the void area are out-of-focus reflections from the bottom of the cavity. The original magnification was 800X. The superimposed line spacing represents 30 microns between lines.

It can be seen by comparison of Figs. 7, 8, and 9 that near-surface porosity was distinctly related to the microstructure. Figures 7, 8, and 9 are all at the same magnification but show the effect of slightly different microstructure. Although in some cases (Fig. 7) the appearance suggests a corrosion problem, this was not the case, since this phenomenon was as common on bare, unused grids as for those in cured or cycled plates. Although cured plates have been found to undergo corrosion because of the alkaline nature of the wet paste, the effect of such an attack is quite different than that seen in Fig. 7. Corrosion during curing brings about an attack only on the lead of the casting so that the antimony is not removed but remains in the corrosion product. The corrosion product from such an attack is also clearly visible in these cases. In the present example the antimony or the eutectic alloy, rich in antimony, is missing at the surface, and there is no evidence of any corrosion product. While anodic attack on lead-antimony alloys removes the antimony in a similar manner, the removal is accompanied by the formation of a corrosion product in the form of PbO_2 . Since these were negative plates and not subjected to the potentials of the positive plate, this effect, when found in cured, formed, or cycled plates, must be due to the same causes that promote its appearance on bare, unused grids.

It would seem that the type of cavities seen in Figs. 7, 8, and 9 is the result of shrinkage of the eutectic portion as it solidified, assuming the nucleation of the eutectic began at some point within the channels and not at the surface.

Fig. 7 - Porous areas near the surface of the casting, showing the complete lack of antimony particles in this area and that voids align with remaining antimony particles. The particles seen in the dark areas to the right of the grid surface are lead dendrites of the negative active material. The original magnification was 400X. The superimposed line spacing represents 60 microns between lines.



Fig. 8 - Another example of porous area near surface. A different alloy structure and larger void spaces are shown here. The original magnification was 400X. The superimposed line spacing represents 60 microns between lines.

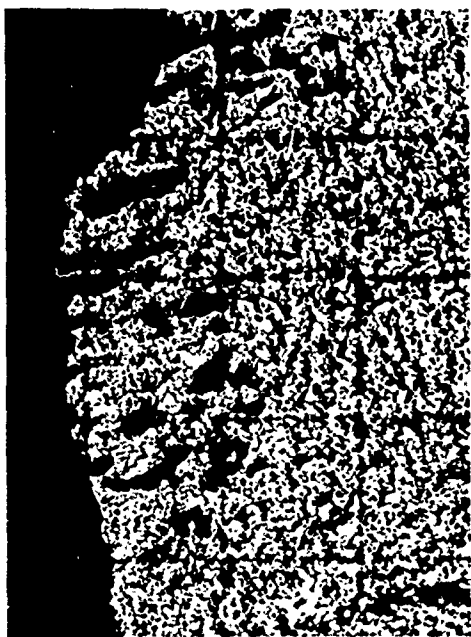


Fig. 9 - Another example of a porous area near the surface. This figure shows a slightly different alloy structure and type of porosity. The original magnification was 400X.

In a previous report (2) it was emphasized that, as a result of inverse segregation, the surface of the grid (as seen in cross section) is outlined by a regular row of antimony particles. Figures 7 and 9 show no such line of particles at the surface, suggesting that this portion of the cast section may have been at the highest relative temperature during freezing and that it thus acted as the sprue for the remainder of the section. If this were true, metal would be withdrawn from this area during the freezing of the eutectic portion in other parts of the section and porosity might occur as seen here. Figure 8 has this line of antimony particles along the surface, however, suggesting that some other explanation is necessary. Figure 8 appears to be the result of a slightly different mechanism in any case, since the porosity does not seem to extend quite to the surface. Nevertheless, the voids did extend to the surface, because they had become filled with the impregnating plastic. Figure 8 particularly emphasizes the interdendritic nature of the process. The metal structure shown in Fig. 9 has a lower antimony content than the other two and appears to have a slightly distorted structure, possibly because the metal was already in the process of freezing as it was forced into this mold section.

A very puzzling feature of the type of microporosity shown in this report is the manner in which it is concentrated in certain areas while no porosity will be found elsewhere in the cross section. Figure 10 shows an area of porosity with well-defined boundaries in which almost every dendritic channel consists of a void. The presence of the impregnating plastic which fills the voids proves that the void also connects with the surface in some other plane. Despite the relatively large size and severe microporosity shown here, the remainder of the cross section appeared to be absolutely free of defects.

A few examples of microporosity were also found that did not require a particular type of microstructure for their existence and which did not always show a clear relationship with the interdendritic channels. In Fig. 11, for example, the bright antimony particles appear quite random, and they do not seem to outline any particular dendritic structure, yet quite large voids appear. These large voids do not seem to have any particular relation to the microstructure surrounding them and do not seem to be formed in dendritic channels. The thin filaments of metal within the voids do suggest a withdrawal of surrounding metal at some stage of freezing.

Fig. 10 - An example of the manner in which porous areas usually occur in the interior of the casting. The pores all interconnect, and adjoining areas are completely free of porosity. The original magnification was 250X. The superimposed line spacing represents 95 microns between lines.



Fig. 11 - An example of the large voids sometimes found which seem to bear no relation to the surrounding microstructure. The original magnification was 400X. The superimposed line spacing represents 60 microns between lines.

On the other hand, the voids that appear in Fig. 12 do suggest some sort of channels, although their general size and configuration indicate a structure of a size with which the scattered antimony particles do not appear to agree. Figure 13 shows a large cavity in a nearly pure lead casting. In this case there would be no temperature differential such as would exist in an alloy, although the metal would certainly supercool to some extent before nucleation occurred. Because of such supercooling the metal would consist of a very complex dendritic structure in which the dendritic arms of individual crystals would be parallel and closely spaced, with all solidification taking place at practically no temperature gradient. Despite these conditions a large void had formed which also was connected with the surface, as shown by the presence of the impregnating plastic. Such a large void as shown here is definitely not in character with a metal structure such as just proposed and does not suggest that metal has withdrawn along interdendritic channels to form a cavity. A bright area at the top of the cavity shown in the photograph is caused by a small amount of corrosion product that was found in the pore. A similar area appears near the bottom of the photograph.

Although there seems to be no evidence that gas is dissolved in molten lead alloys, it is still possible that bubbles of gas might have become entrapped somewhere in the mold, and subsequently in the casting, while the metal was being introduced. If this were the case, the entrapped gas could conceivably escape to the surface by pushing the still molten metal of the channels ahead of it and thus leave a void in the channel which would remain connected to the surface. Such a supposition raises problems, however. Why,



Fig. 12 - Another example of large voids, suggesting channels in the metal but bearing little relation to the surrounding microstructure. The original magnification was 400X.



Fig. 13 - A large void such as commonly seen in lead metal castings. Here there is no antimony to outline the primary dendrites, but the hole is large in relation to the microstructure that was subsequently revealed by etching. The bright area near the top of the void is either a dross or oxide inclusion or perhaps some corrosion product produced during cell operation. The original magnification was 400X.

for example, should such escape take place only after primary crystallization had occurred when it would appear much easier for the gas bubble to escape while the whole mass was molten? On the other hand, grid castings larger than the automotive type used in this study are often found to contain a porous or completely open channel along the center line of the grid member. This occurs at the point where the temperature would probably have been the highest and at the point where the metal would have remained molten for the longest time. In other words, metal would have been withdrawn from this point to feed the solidification in areas nearer to the surface of the cast section.

It seems very likely that commercial molds do not operate at a completely uniform temperature all along the mold face; in fact, the possibility is extremely improbable. In addition, the configuration of the grid causes varying amounts of molten metal to be collected in different parts of the mold cavity, which will also contribute to unequal freezing. At any grid cross section that maintained a slightly higher temperature than the surrounding sections, conditions would be set up favorable for withdrawal of metal from this section to feed adjoining cross sections.

In large metal castings the weight of the remaining liquid portion usually causes the shrinkage effects to be concentrated at the top of the casting or in the pouring gate. It may be true that the micropores under discussion are also concentrated in areas that would be at the top of the grid cross section during the casting operation, but the random method used in cutting samples made this point impossible to check. However, considering the small section presented by individual grid members and the possibility of open channels throughout the casting that could be influenced by gravitational flow, this possibility does not seem likely. It is more likely that relatively small areas with short capillaries would be involved. In this case surface tension could easily overcome gravitational forces, and metal withdrawal could occur from a hotter area regardless of its relative position in the cross section. The often-repeated observation of porosity in the grids being much greater at points where two grid members intersected supported this assumption. An example of this behavior would be where the staggered horizontal bars of the plate intersected the heavier, vertical supporting grid bars. At such areas there is a larger mass of metal with consequent slower cooling, and metal is withdrawn from these points to feed more rapidly solidifying adjacent areas.

A supposition such as the above does not necessarily require that the voids that do form should be connected with the surface of the casting, since presumably the surface of the casting would have frozen first. Almost invariably, however, the impregnating plastic was found in the voids.

POSSIBILITY OF ADDITIONAL POROSITY

In addition to the microporosity already discussed, which produces voids of a size easy to detect and which are usually concentrated in one area of the cross section, a much more uniformly distributed porosity could occur, which might well be of much smaller dimensions, of the order of micron or less.

Figure 14 shows a phenomenon that is seen quite often when the dry-polishing, no-etching technique is employed. The boundary between the two grains (arrow) appears quite dark and rather broad. This boundary was at first dismissed as being a characteristic caused by differing levels of relief between the two grains or the familiar notching that occurs at the grain boundaries, combined with an illusion caused by the method of illumination. Examination at a much higher magnification, however, confirmed the reality of the dark boundary area (Fig. 15). The printed reproduction of this photograph may not be able to show that this darkly shadowed area was composed of a large number of very small individual dark spots that varied considerably in size and shape. The exact nature of these dark spots has not been determined, but it is suspected that they are indeed very small voids and that the grain boundary in this case is very porous.

Fig. 14 - An area of grain-boundary porosity. Note the dark, broad boundary between the upper and lower grain, which gives a porous appearance. The original magnification was 150X.

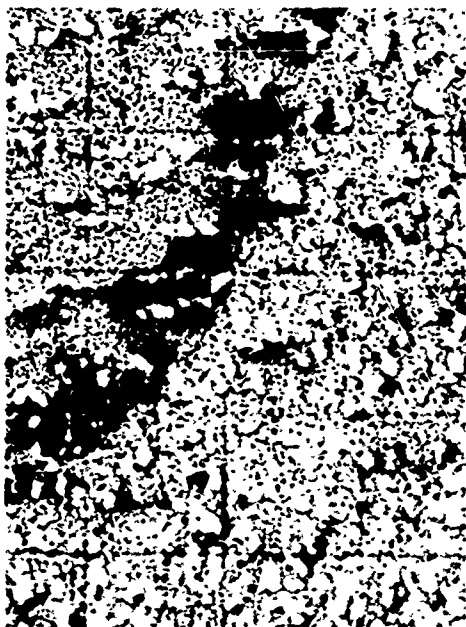
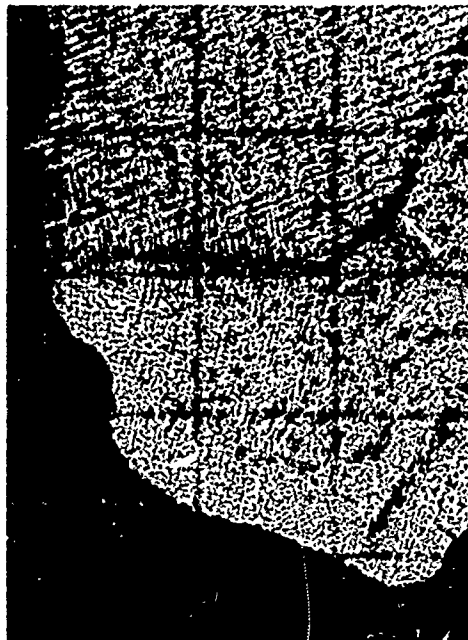


Fig. 15 - A much enlarged view of the same grain boundary as in Fig. 14. The dark spots may represent very small pores; these spots become more numerous at the grain boundary. The original magnification was 800X.

The area shown in Fig. 16 shows actual voids of fairly large size such as have been illustrated in previous figures. The smooth almost featureless areas surrounding these voids are the primary lead dendrites. But notice the many dark areas that are not large voids but are made up of the small black spots previously referred to. What is most significant is that these small black spot areas have a general shape much like that of the voids. In other words, they appear to follow the interdendritic channels, while the primary lead, identified as the lighter, smooth areas between the dark shows hardly any of these black spots.



Fig. 16 - Another illustration of the black spots that may represent very small pores in the metal. The lighter, pore-free areas are primary lead crystals. Areas which contain the small dark spots represent the channels where the eutectic filled the spaces between the primary crystals. Note the similarity of these areas to that of the actual voids near the center of the photograph. The original magnification was 1600X. The superimposed line spacing represents 15 microns between lines.

While the dark particles might actually be the result of an impurity, either itself dark colored or easily converted to a dark colored oxide, it seems more likely that they are not particles at all but small pits or pores. Replication of the surface and examination of the replica by the electron microscope might be able to resolve this question but to so mount the specimen as to make possible the type of fine polishing required and at the same time be able to remove a replica intact has so far not been found to be practical.

In any case, it seems logical to expect the presence of such very small pores. There is a well-known discrepancy between the theoretically calculated density and that found by actual measurement. In the final solidification of the eutectic crystal, lamellae of both lead and antimony are crystallizing simultaneously and side by side, with a reduction in volume accompanying the process. It is inconceivable that such a process can occur without the generation of innumerable small voids around the solidifying crystals.

Whether because of porosity, areas of microimpurity, or some other cause, the areas delineated by the dark spots are those that corrode at the fastest rate and along which corrosion penetrates to much greater depths than in the surrounding primaries. This behavior would be expected in a very porous area.

Whether or not this latter type of porosity actually does exist and is represented by the dark spots in the metallographic section, there can be no doubt that the porosity referred to in the earlier part of this report does exist. There is likewise no doubt that such porosity is an extremely common occurrence in grid castings.

CONCLUSIONS

The lead-antimony system is generally regarded as one of the easiest lead alloys to cast. Yet in such a system a very high order of microporosity has been found, much more so than had been previously realized. Since these porous areas were almost invariably found to be connected to the surface of the casting, it is almost a certainty that all penetrating types of corrosion are initiated in such cavities. It seems obvious that such random porosity, with its accompanying corrosion, makes corrosion tests based on weight loss or depth of penetration practically without meaning. The presence of such random porosity also explains the inability to make significant corrosion tests on small collections of statistics. If such a large amount of porosity is present in an alloy considered relatively easy to cast, the porosity in many of the alloys that have been tested as alternates must have been of a much higher order. This raises the question whether porosity or actual corrosion resistance was in fact the criteria for such tests.

Microporosity may also explain the puzzling fact that many preliminary corrosion tests which have uncovered apparently superior corrosion resistant alloys later failed miserably in tests in actual cells. Most of such preliminary tests are made on simple rectangular or cylindrical cast bars with a relatively larger cross section than that found in actual grid members. Such castings also tend to freeze more slowly and more uniformly than do grid castings. Gravitational flow of the eutectic through the channels between the primaries is much more pronounced. Simply stated, the preliminary test pieces were by all odds much less porous than the subsequently tested grid castings.

The elimination of the microporosity discussed in this report is not easy. A possible solution might be to increase the antimony content. This would result in smaller and much simpler primary lead dendritic crystals and a much larger proportion of the lower freezing eutectic, providing larger channels and less obstructed flow during eutectic freezing. This solution is unsatisfactory, because economic demands require alloy of low antimony content and also because possible benefit in increased flow would be largely offset by a reduced freezing range.

The principal hope for the elimination of porosity appears to be in the elimination of supercooling and the consequent intricate dendritic structure. Some progress in this direction has been made in other alloy systems, notably aluminum, where higher melting heterogeneous nuclei have been introduced into the alloy and/or presented at the mold surface to induce more rapid nucleation. Supersonic vibration has also been used with some success.

It should also be realized, however, that without the primary intricate dendritic crystallization that locks the lead into immobilized position, it would be extremely difficult to prevent the separation of the lead and antimony into two layers. This separation would occur as the much heavier lead crystals sank to the bottom and the lighter antimony crystals rose to the top. Without supercooling the process of casting would also become more difficult.

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<p>Microscopic examination of over two-thousand grid cross sections, which had been obtained from the product of many different manufacturers, indicated that grid microporosity was very high. Using magnification as low as 45X, microporosity was found in 20% of the grids by random sampling. Examination at higher magnification showed much more microporosity to be present, and it is estimated that 40 to 50% of the cross sections would have been found to be porous if examined at higher magnification (800-1000X). Since the sampling was random, it is very probable that all of the cast grids had porosity at one or more points which could contribute to premature failure by corrosion.</p>		

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